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(21) International Application Number: PCT/US90/03681 (22) International Filing Date: 28 June 1990 (28.06.90) (30) Priority data: 372,986 28 June 1989 (28.06.89) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US). (72) Inventor: TSE, Mun, Fu ; 1706 Fair Oaks Drive, Seabrook, TX 77586 (US). (74) Agents: KURTZMAN, Myron, B. et al.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522-5200 (US).		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: BLOCK COPOLYMER ADHESIVES IN HOT MELTS AND POLYESTER LAMINATES (57) Abstract <p>Disclosed are laminates and hot melt adhesive formulations containing dihydrocarbyl azodicarboxylate-modified multi-block copolymers. The copolymer contains terminal non-elastomeric polymonovinylarene blocks and a non-terminal elastomeric block of conjugated diene. The unmodified multiblock copolymer has a molecular weight of from 20,000 to 250,000, and the elastomeric block comprises from 40 to 90 weight percent of the unmodified block copolymer. The block copolymer is modified by reaction with from 10 to 100 weight percent, especially from 20 to 80 weight percent, on a basis of the unmodified elastomeric block of a dihydrocarbyl azodicarboxylate to obtain a modified multiblock copolymer wherein the elastomeric block contains pendant bicarbamate moieties. The hot melt adhesive composition includes the multiblock copolymer and a compatible tackifier at a ratio of tackifier to copolymer of from 10:90 to 90:10 and may also include up to 40 weight percent of an oil of the copolymer and tackifier. The laminate has at least one polyester substrate to which the adhesive composition is adhered.</p>		

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BLOCK COPOLYMER ADHESIVES IN HOT MELTS AND POLYESTER LAMINATES.

Field of the Invention

The present invention relates to block copolymer adhesives having enhanced adhesion to polyester substrates, and more particularly to hot melts and polyester laminates containing modified multiblock copolymer adhesives.

Background of the Invention

Multiblock copolymers having non-elastomeric terminal blocks and an elastomeric non-terminal block are well known from the prior art. Such block copolymers include, for example, polystyrene-polyisoprene-polystyrene and polystyrene-polybutadiene-polystyrene. Because these polymers exhibit both thermoplastic properties owing to the thermoplastic end blocks, as well as elastomeric properties due to the elastomeric internal block, they have found a wide variety of commercial applications. One such commercial application employs the multiblock copolymer in a blend with a tackifying resin for pressure sensitive adhesive compositions. The composition is typically applied to a film or other substrate to adhere the film or substrate to yet another substrate in a laminated structure.

One drawback of the prior art multiblock copolymer adhesive compositions is that the multiblock copolymers generally have poor adhesion to polar substrates such as polyester. Another drawback has been that the multiblock copolymer-based hot melt compositions have a relatively high melt viscosity and must generally be used with solvents or at undesirably high temperatures. There remains a need for multiblock copolymers with improved adhesion to polyester films and other substrates made of polyester, and/or with reduced melt viscosity.

It is known from U. S. Patent 4,255,536 to Udipi to modify copolymers of a conjugated diene and a monovinylarene, such as styrene-butadiene-styrene teleblock copolymer, by reaction with a dihydrocarbyl azodicarboxylate such as dimethyl azodicarboxylate or di-t-butyl azodicarboxylate, to obtain a modified copolymer which can be compounded and cured into a tire tread composition stated to have improved oil resistance and wet skid resistance.

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1 The isopropyl azodicarboxylate modification of polybutadienes
2 is described in Schulz et al, Macromolecules, vol. 13, pp. 1367-1375
3 (1980); Spiewak et al, Journal of Applied Polymer Science, vol. 26,
4 pp. 4331-4334 (1981); and Hamed et al, Polymer Bulletin, vol. 9,
5 pp. 525-532 (1983). The modified polybutadienes are stated to have
6 good green strength, cohesive strength and autohesion properties.

7 Other references describing crosslinking and other reactions of
8 polymers with azo compounds include U. S. Patent 4,129,531 to Rauer
9 et al; 2,994,357 to Serniuk et al; and 4,791,174 to Bronstert et al.

10 Summary of the Invention

11 The present invention provides a laminate containing at least
12 one polyester substrate and an adhesive layer in contact with the
13 polyester substrate. The adhesive layer comprises a dihydrocarbyl
14 azodicarboxylate-modified multiblock copolymer having terminal
15 non-elastomeric polyvinylaromatic blocks and a non-terminal
16 elastomeric block of polymerized polyene. The block copolymer is
17 modified by reaction of the elastomeric block with, for example,
18 from 10 to 100 weight percent, especially from 20 to 80 weight
19 percent, based on the weight of the unmodified elastomeric block, of
20 a dihydrocarbyl azodicarboxylate. The resulting modified copolymer
21 has pendant bicarbamate groups along the elastomeric block. The
22 laminate may further include another substrate in contact with the
23 adhesive layer, and the laminate exhibits a cohesive failure mode at
24 the adhesive layer.

25 The present invention also provides a hot melt adhesive
26 composition which can be used for pressure sensitive adhesive
27 applications. The hot melt adhesive composition contains from 10 to
28 90 parts by weight of a dihydrocarbyl azodicarboxylate-modified
29 multiblock copolymer, from 90 to 10 parts by weight of a tackifier
30 compatible therewith, and zero to 40 parts by weight of a mineral
31 oil. The multiblock copolymer has terminal non-elastomeric blocks
32 of polyvinylarene and a non-terminal elastomeric block of
33 polymerized conjugated diene. The multiblock copolymer is modified
34 by reaction with a dihydrocarbyl azodicarboxylate.

35 Detailed Description of the Preferred Embodiments

36 The laminate of the present invention contains at least a first
37 substrate of polyester and at least one modified multiblock

1 copolymer adhesive layer in contact therewith. The laminate may
2 include a plurality of substrates which are solid, usually and
3 preferably in the form of films, sheets and the like. A second
4 substrate in contact with the adhesive layer opposite the first
5 polyester substrate may be a polyester substrate, or may be made of
6 another material, such as, for example, wood, metal, glass,
7 thermoset polymer, or thermoplastic polymer. In a preferred
8 embodiment, a second substrate in contact with the modified
9 multiblock copolymer adhesive layer is a thermoplastic so that the
10 laminate is reprocessible. Thermoplastic polymers include both
11 polar and non-polar polymers. As examples of non-polar
12 thermoplastics, there may be mentioned polyolefins such as
13 polypropylene, high density polyethylene, low density polyethylene,
14 linear low density polyethylene, other polymers such as polystyrene,
15 and the like. As examples of polar thermoplastics, there may be
16 mentioned polyester, polyamide, polyvinyl chloride, polyvinylidene
17 chloride and the like. In a preferred embodiment, the laminate
18 comprises a polyester sheet or film as a first substrate and a
19 polyester or nonpolyester sheet or film as a second substrate, and
20 the modified multiblock copolymer adhesive composition in a layer
21 between the first and second substrates for bonding the first and
22 second substrates together.

23 The multiblock copolymers which are modified for use in the
24 laminates and hot melts of the present invention are well known and
25 are commercially available. The copolymer has terminal or end
26 blocks of non-elastomeric polymerized vinylaromatic, preferably
27 monovinylarene, and at least one non-terminal block of elastomeric
28 polymerized polyene, preferably conjugated diolefin. These block
29 copolymers typically come in three-block, five-block and starblock
30 configuration with a molecular weight of from 20,000 to 250,000,
31 preferably from 40,000 to 200,000, and a diolefin content of from 40
32 to 90 weight percent, preferably from 57 to 86 weight percent.
33 Commercially, the non-elastomeric blocks are usually polystyrene,
34 poly(α -methylstyrene), and poly(styrene/ α -methylstyrene), but
35 there may also be mentioned terminal blocks containing other
36 suitable polymerized monomers, such as, for example, acenaphthylene,
37 vinylnaphthalene, isopropenylnaphthalene, 4-phenylstyrene,

1 4-tert-butylstyrene, 4-isopropylstyrene, 4-methoxystyrene,
2 2-vinylpyridine, 2-methyl-5-vinylpyridine, vinylxylene,
3 ethylvinylxylene, methylvinylxylene, and the like. The terminal
4 blocks may also include interpolymers and block polymers formed from
5 two or more of such monomers, or the tapered blocks comprising one
6 of the vinylaromatic monomers and one of the conjugated diolefin
7 monomers (minor component).

8 The elastomeric block or blocks may be a homopolymer of any
9 conjugated diolefin having up to 12 carbon atoms, preferably 4-8
10 carbon atoms, or a block copolymer or interpolymers of two or more
11 such diolefins. Polybutadiene and polyisoprene are common, but
12 there may also be mentioned other suitable monomers which may be
13 polymerized in the elastomeric block, such as, for example,
14 dimethylbutadiene, piperylene, phenylbutadiene, and the like.

15 The multiblock copolymer is modified by reaction with a
16 dihydrocarbyl azodicarboxylate. The modification may be effected by
17 contacting the multiblock copolymer with the dihydrocarbyl
18 azodicarboxylate at effective reaction conditions. The dihydrocarbyl
19 azodicarboxylates suitable for modification of the multiblock
20 copolymer include the azo esters of the following formula:



23 in which R^1 and R^2 are independently alkyl, cycloalkyl, aryl or
24 combination radicals and can be the same or different. Typically
25 R^1 and R^2 each contain from 1 to 12 carbon atoms. Preferred are
26 the azodicarboxylates wherein R^1 and R^2 are selected from
27 methyl, ethyl, isopropyl, t-butyl, cyclohexyl, phenyl, and the
28 like. Dialkylazodicarboxylates, especially isopropylazodi-
29 carboxylate, are particularly preferred.

30 A method for the reaction between the dihydrocarbyl
31 azodicarboxylate and the multiblock copolymer is described, for
32 example, in aforementioned U. S. Patent 4,255,536, which is hereby
33 incorporated herein by reference. Briefly, the multiblock copolymer
34 may be reacted in a suitable solvent with the dihydrocarbyl

1 azodicarboxylate in suitable amounts at moderately elevated
2 temperatures below about 150°C, for a period of time from about 0.1
3 hours to several days or more under an inert atmosphere at
4 atmospheric or superatmospheric pressure. Preferred amounts of the
5 dihydrocarbyl azodicarboxylate are in the range of from 10 to 100
6 percent by weight of the diene content of the block copolymer, and
7 especially from 20 to 80 weight percent. The modified multiblock
8 copolymer contains pendant bicarbamate moieties along the length of
9 the polydiene chain, while the polyvinylarene blocks are essentially
10 unmodified. The modified copolymer may be recovered by evaporation
11 of the solvent or by precipitation with an antisolvent and
12 filtration, although it is contemplated that the solution resulting
13 from the reaction mixture may be used to cast the adhesive layer
14 directly onto a substrate.

15 The dihydrocarbyl azodicarboxylate-modified block copolymer may
16 be used as an adhesive layer in the polyester laminate by
17 conventional laminating techniques, such as, for example,
18 coextrusion, extrusion coating, solution coating, and the like. In
19 a preferred embodiment, the block copolymer is applied to the
20 substrate as a hot melt adhesive containing the modified block
21 copolymer and a compatible tackifier. The tackifiers typically have
22 a softening point of from 70° to 130°C, preferably from 80° to
23 110°C; a number-average molecular weight of from 500 to 1300,
24 preferably from 700 to 1300; a weight-average molecular weight of
25 from 1000 to 3000, preferably from 1200 to 2500; an acid number of
26 from 0 to 50; a bromine number of from 5 to 30; and a specific
27 gravity of from 0.80 to 1.30. As suitable tackifiers there may be
28 mentioned rosin esters, terpene-phenolic resins and mixed aliphatic-
29 aromatic resins, well known in the art. Exemplary rosin esters
30 include those available under the trade designations Foral,
31 Pentalyn, Permalyne, Bevilite, Bevitack, Zonester, Dertolyne,
32 Granolite, Tergum, Resiester, Unitac, Oulutac, etc. Exemplary
33 terpene-phenolic resins include those available under the trade
34 designations Dertophen, Uravar, Nirez V, etc. Exemplary mixed
35 aliphatic-aromatic resins include those available under the trade
36 designations Escorez, Regalite, Hercures AR, Imprez, Norsolene M,
37 Marukarez, Arkon M, Quintone, etc. Other tackifiers may also be

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1 employed, provided they are compatible with the nonterminal block of
2 the modified block copolymers.

3 The weight ratio of tackifier to modified block copolymer may
4 be from about 10:90 to 90:10, preferably from 20:80 to 80:20, and
5 especially from 30:70 to 70:30.

6 Mineral oil is desirably used in the hot melt adhesive
7 composition when ambient temperature tack is desired, for example,
8 in pressure sensitive hot melt adhesives. Depending on the nature
9 and amount of the tackifiers used, the oil may comprise from zero to
10 40 weight percent of the adhesive composition, preferably from 5 to
11 20 weight percent of the adhesive composition. The hot melt
12 composition may also include conventional additives such as
13 pigments, fillers, antioxidants, stabilizers, and the like, in
14 conventional amounts, but the hot melt is preferably essentially
15 free of solvents. Antioxidants such as Irganox 1010, when used, are
16 typically present at 0.5 weight percent of the hot melt adhesive
17 composition.

18 The hot melt adhesive is prepared by conventionally melt
19 blending the components together at elevated temperatures (from
20 about 150°C to about 200°C) under an inert gas blanket until a
21 homogeneous mix is obtained. Any mixing method producing
22 homogeneous blend without degrading the hot melt components is
23 satisfactory. One well known method to the art of blending
24 materials of this type is to carry out the hot melt blending in a
25 heated vessel equipped with a stirrer.

26 The hot melt adhesive, in addition to having enhanced adhesion
27 to polyester and other polar polymeric substrates, has the further
28 advantage that the hot melt composition has a reduced viscosity
29 relative to hot melt adhesives prepared from similar but unmodified
30 multiblock copolymers. As a result, the present hot melt adhesive
31 leads itself to improved processability, permitting lower
32 temperatures to be used, and avoiding the necessity for solvents or
33 other viscosity-reducing additives.

34 The invention is illustrated by way of the following examples.
35

36 Example 1

37 A polyester laminate was prepared and evaluated using a
styrene-isoprene-styrene block copolymer (SIS) which was modified

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with isopropyl azodicarboxylate (IAD). The SIS was obtained commercially under the designation Kraton 1107 and contained 86 weight percent isoprene and had a number average molecular weight (M_n) of 110,000 and a ratio of weight average molecular weight (M_w) to M_n of 1.61. The SIS was modified with IAD by dissolving 20 weight percent SIS in hot benzene or toluene solution in a nitrogen purged reaction vessel. The SIS solution was cooled to ambient temperature, and a 10 weight percent solution of IAD in benzene or toluene was added in a quantity corresponding to 30 percent by weight of the SIS isoprene content. The solution was then stirred, heated and maintained at reflux conditions at about 80°C for benzene and about 110°C for toluene under a nitrogen purge for 24 hours. Reaction was evidenced by a reduction in the yellow color of the reaction solution with the passage of time. The IAD-modified SIS was recovered by precipitation with methanol, filtration and drying in a vacuum oven at 50°C overnight. The IAD-modified SIS had viscoelastic loss peaks as determined on a Rheometrics System IV spectrometer at -44°C and 112°C, as compared to the same peaks at -59°C and 121°C for the unmodified SIS. The IAD-modified SIS had an M_n of 141,000 and an M_w/M_n ratio of 1.62. A polyester laminate was prepared by compression of a 4 mil thickness of the IAD-modified SIS between 4 mil Mylar polyester films at 180°C using 40 psi for 5 minutes. The laminate was cut into 1-inch wide strips and subjected to T-peel strength testing at 2 inches/minute. The laminate made with the IAD-modified SIS had a peel strength of 5.7 lb/in. and exhibited a cohesive failure mode, while the identically prepared laminate made with the unmodified SIS had a peel strength of 4.2 lb/in. and exhibited an adhesive failure mode. Viscosity results are as follows:

Temperature (°C)	Viscosity (Poises)	
	Unmodified Polymer	Modified Polymer
120	2.9×10^5	1.0×10^5
140	1.5×10^5	0.5×10^5
160	7.7×10^4	2.9×10^4

Example 2

Laminates were prepared as in Example 1 using Kraton 1102

1 styrene-butadiene-styrene block copolymer (SBS) containing 72 weight
2 percent butadiene. The unmodified SBS had an M_n of 67,000 and an
3 M_w/M_n ratio of 1.45. Following modification with 30 weight
4 percent IAD based on the butadiene weight, as described in Example
5 1, the IAD-modified SBS had an M_n of 74,000 and the M_w/M_n
6 ratio was unchanged. The IAD-modified SBS had viscoelastic loss
7 peaks at -60°C and 81°C , compared to -82°C and 87°C for the
8 unmodified SBS. Mylar polyester laminates prepared as described in
9 Example 1 with the IAD-modified SBS had a peel strength of 9.0
10 lb/in. and exhibited a cohesive failure mode, compared to a peel
11 strength of 2.0 lb/in. and an adhesive failure mode for the
12 identically prepared laminates using the unmodified SBS.
13 Viscosities at 120°C are 3.7×10^5 poises and 1.5×10^5 poises
14 for the unmodified and modified polymers, respectively.

15 Examples 3 and 4

16 The procedures of Examples 1 and 2 were followed to prepare
17 laminates of 4 mil aluminum foil. Both the IAD modified copolymers
18 and the unmodified copolymers exhibited an adhesive failure mode.
19 The unmodified SIS laminate had a better peel strength of 8.4
20 lb/in., compared to 6.9 lb/in. for the IAD-modified SIS. The
21 IAD-modified SBS, however, had a peel strength of 9.8 lb/in.
22 compared to 8.6 lb/in. for the unmodified SBS.

23 Example 5

24 A polyester laminate was prepared and evaluated using a tapered
25 styrene-butadiene-styrene block copolymer (SBS) which was modified
26 with isopropyl azodicarboxylate (IDA). The SBS was obtained
27 commercially under the designation Stereon 840A and contained 57
28 weight percent butadiene and had a number-average molecular weight
29 (M_n) of 60,000 and an M_w/M_n ratio of 2.0. Identical reaction
30 conditions as in Example 1 were used to modify the polymer except
31 that the amount of IAD added was in a quantity corresponding to 20
32 percent by weight of the SBS butadiene content. The hot melt
33 adhesive was then prepared by melt blending 60 weight percent of
34 Foral 105, 30 weight percent of the modified Stereon polymer, and 10
35 weight percent of mineral oil (Kaydol[®] from Witco Chemical
36 Corporation) at 180°C under a nitrogen blanket. A 0.5 weight

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1 percent of an Irganox 1010 stabilizer based on the total hot melt
2 blend was added to the formulation. A polyester laminate was
3 prepared by compression of a 6 mil thickness of the formulated
4 adhesive based on this IDA-modified Stereon polymer between 4 mil
5 Mylar polyester film at 150°C using 40 psi for 10 seconds. The
6 laminate was cut into 1-inch wide strips and subjected to T-peel
7 strength testing at 2 inches/minute. The laminate had a peel
8 strength of 7.8 lb/in. and exhibited a cohesive failure mode. The
9 adhesive material itself showed pressure sensitive tack. The
10 laminate containing the identical formulation based on the
11 unmodified block copolymer had a peel strength of 4.7 lb/in. and
12 exhibited a cohesive failure mode.

13 Example 6

14 The procedures of Example 5 were followed to prepare laminate
15 of 4 mil polyester film except that Foral 105 was replaced by
16 Bevilite 62-85 in the hot melt blend composition. The laminate had
17 a peel strength of 6.6 lb/in. and exhibited a cohesive failure
18 mode. The adhesive material itself showed pressure sensitive tack.
19 The laminate containing the identical formulation based on the
20 unmodified block copolymer had a peel strength of 4.4 lb/in. and
21 exhibited a cohesive failure mode.

22 The foregoing is illustrative and explanatory of the invention,
23 and many variations in the specific details thereof will become
24 apparent to those skilled in the art in view thereof. It is
25 intended that all such variations within the scope or spirit of the
26 appended claims be embraced thereby.

CLAIMS:

1. Polyester laminate, comprising:
a first polyester substrate; and
an adhesive composition adhered thereto, said
adhesive composition comprising a multiblock
copolymer having terminal nonelastomeric
polyvinylaromatic blocks and a non-terminal
elastomeric block of polymerized polyene modified by
reacting said elastomeric block with a dihydrocarbyl
azodicarboxylate.
2. Laminate according to claim 1, wherein said
dihydrocarbyl azodicarboxylate is a dialkyl azodicarboxylate,
wherein said multiblock copolymer has a molecular weight of from
20,000 to 250,000; wherein said elastomeric block comprises from
40 to 90 weight percent of said multiblock copolymer, and/or
wherein said multiblock copolymer contains from 10 to 100 weight
percent, especially from 20 to 80 weight percent, dihydrocarbyl
azodicarboxylate on the basis of the unmodified elastomeric block.
3. Laminate according to claim 1 or claim 2, wherein
said non-elastomeric blocks comprise polymerized monomer selected
from the group consisting of styrene, α -methylstyrene,
acenaphthalene, vinyl naphthalene, isopropenyl naphthalene,
4-phenylstyrene, tert-butylstyrene, 4-isopropylstyrene,
4-methoxystyrene, 2-vinylpyridine, 2-methyl-5-vinylpyridine,
vinylxylene, ethylvinylxylene, methylvinylxylene, vinyltoluene,
and mixtures thereof, or one of the above with minor or minute
amounts of one of the conjugated diolefin monomers, especially
butadiene or isoprene.

4. Laminate according to any of the preceding claims, wherein said elastomeric block comprises polymerized $C_4 - C_{12}$ conjugated diolefin, preferably polymerized $C_4 - C_8$ conjugated diolefin and especially a polymerized diene selected from the group consisting of butadiene, isoprene, dimethyl butadiene, piperylene or phenylbutadiene or mixtures thereof.

5. Laminate according to any of the preceding claims, wherein said polyvinylaromatic comprises polymonovinylarene.

6. Laminate according to any of the preceding claims, wherein said adhesive composition further comprises a tackifier preferably selected from resin esters, terpene phenolic resins and mixed aliphatic-aromatic resins, compatible with said multiblock copolymer at a weight ratio of tackifier:copolymer of from 10:90 to 90:10, preferably from 20:80 to 80:20 and especially from 30:70 to 70:30.

7. Laminate according to claim 6 further comprising from zero to 40 weight percent of oil of said copolymer and said tackifier; and/or further comprising from 5 to 20 weight percent of mineral oil of said copolymer and said tackifier.

8. Laminate according to any of the preceding claims further comprising a second substrate adhered to said first substrate by said adhesive composition, preferably a thermoplastic polymer and especially polyester.

9. Laminate according to any of the preceding claims in which the dihydrocarbyl azodicarboxylate has the formula:



wherein R^1 and R^2 are independently alkyl, cycloalkyl, aryl or combination radicals containing from 1 to 12 carbon atoms, preferably with R^1 and R^2 are alkyl and especially with R^1 and R^2 are isopropyl.

10. A hot melt adhesive composition, comprising:
from 10 to 90 parts by weight of a multiblock copolymer modified by reaction with a dihydrocarbyl azodicarboxylate, wherein said multiblock copolymer comprises terminal nonelastomeric blocks of polyvinylarene and a nonterminal elastomeric block of polymerized conjugated diene; and
from 90 to 10 parts by weight of a tackifier compatible therewith.

11. Composition according to claim 10, wherein said block copolymer contains pendant bicarbamate groups, preferably from 20 to 80 weight percent pendant bicarbamate groups based on the weight of said elastomeric block.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03681

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: B 32 B 7/12, C 09 J 153/02, C 09 J 193/00

II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched ⁷
IPC ⁵	C 08 L, C 09 J
	Classification Symbols

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4255536 (PHILIPS PETROLEUM CO.) 10 March 1981 see claims cited in the application --	1-11
Y	FR, A, 2419311 (SOCIETE KORES HOLDING ZUG AG) 5 October 1979 see claims 1-7; example 1 --	1-11
Y	CA, A, 1114278 (PERMACEL) 15 December 1981 see claims -----	1-11

* Special categories of cited documents: ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
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IV. CERTIFICATION

Date of the Actual Completion of the International Search
27th September 1990

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30. 10. 90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

Natalie Weinberg
Natalie Weinberg

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9003681

SA 38284

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4255536	10-03-81	None	
FR-A- 2419311	05-10-79	AT-A, B 354583 DE-A- 2810532 GB-A, B 2020292	10-01-80 25-10-79 14-11-79
CA-A- 1114278	15-12-81	None	

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